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Diffusion of *n*-Butane/*iso*-Butane Mixtures in Silicalite-1 Investigated Using Infrared Microscopy

Christian Chmelik[1], *Lars Heinke*[1], *Jörg Kärger*[1], *Jasper M. van Baten*[2] *and Rajamani Krishna*[2]

[1] Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, 04103 Leipzig, Germany, E-Mail: chmelik@uni-leipzig.de

[2] University of Amsterdam, Van 't Hoff Institute for Molecular Sciences, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

1. Introduction

Zeolites of MFI-type belong to the most important zeolite structures in catalysis and are used in many shape-selective processes in petroleum refining industry, in particular for the kinetic separation of alkane isomers. Practically all important applications involve mixtures. However, due to the experimental difficulty, the number of experimental studies of mixture adsorption and diffusion is rather small compared to single components.

One of the main advances of the IR microscopy technique (IRM) is the ability to differentiate between different sorbates and to allow, in this way, studies of mixture diffusion. Motivated by the practical relevance, as model system we considered a mixture of a linear and mono-branched alkane in silicalite-1 (MFI-type), viz. *n*-butane (nC4) and *iso*-butane (iC4). The primary objective was to investigate the influence of "intersection blocking" effects [1] on mixture diffusion experimentally.

2. Method

Adsorption and diffusion of nC4/iC4 mixtures in individual silicalite-1 crystals has been investigated at 298 K using infrared (IR) microscopy. To differentiate between nC4 and iC4 in the mixture, nC4 has been used in its fully deuterated form. For calculating the respective intracrystalline concentrations the area under the C-H or C-D stretching vibrations in the IR spectra have been determined, respectively.

3. Results and Discussion

The equilibrium sorption isotherm for a 50:50 gas phase mixture was calculated using Configurational Bias Monte-Carlo (CBMC) simulations. The experimental data of the equilibrium sorption isotherm have been found to be in excellent agreement with the isotherm of CBMC simulations (Fig. 1a). The comparison between simulation results and the experimental data enabled the determination of absolute values of concentration in the IR experiments.

nC4 uptake under presence of iC4 and, vice versa, iC4 uptake under presence of nC4 have been studied experimentally. It is shown that the nC4 counter-uptake (Fig. 1b) is not

limited by the nC4 diffusivity, but by the availability of free sites, which is, in turn, determined by the rate at which iC4 desorbs from the crystal.

The large difference in the diffusivity of nC4 and iC4 by about two orders of magnitude implicates that the much more immobile iC4 is able to "shield" network regions from nC4 by occupying and blocking channel intersections, which act as preferred sites for iC4 [2,3]. A site-percolation threshold, given by the number of iC4 molecules blocking the 'traffic junctions' of the channel network, is employed for explaining the occurrence of network regions which are initially inaccessible for nC4 in the counter-uptake process [3].

The reported work is relevant not only in the modelling and design of zeolite membrane permeation processes, but also for catalytic processes in which one of the reactants (such as iso-alkanes, or benzene) is located preferentially at the intersections of MFI-type crystals [4].

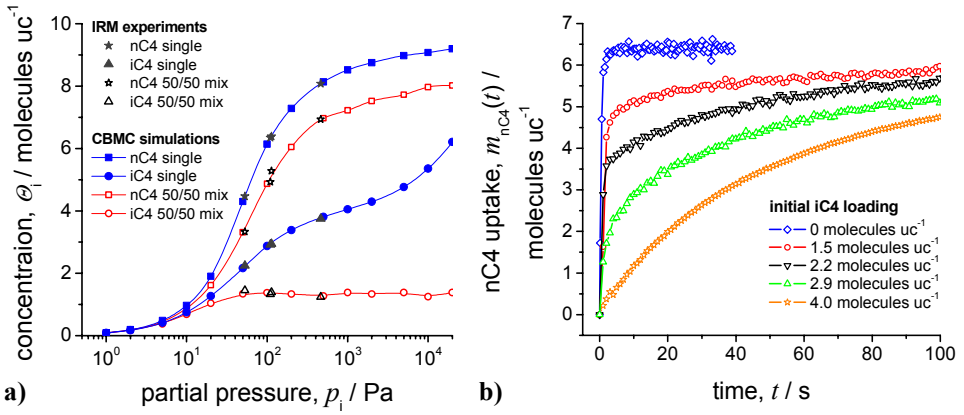

Fig. 1: **a)** CBMC isotherms for single components (connected full symbols) and 50:50 gas mixture (connected open symbols) of nC4 and iC4 in silicalite-1. The simulations are compared with experimental results obtained by IRM. **b)** Impact of different initial iC4 loadings on the 'counter-uptake' of nC4. The rate of nC4 is determined by the availability of free sites, i.e. by the release of iC4.

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